# Summary of MC252 Crude Oil and Vapor Phase Sampling May 17, 2010

## Description of the MC252 Crude

Sample results from the Deepwater Horizon crude oil spill show that the crude oil type can be classified as a "light sweet crude". *Light sweet crude oil* is the form of petroleum that oil refineries prefer because it contains exceptionally high amounts of the chemicals needed to produce gasoline, kerosene, and high-quality crude oil. "Sweet" is a description of how much sulphur is in the oil. "Sweet" crude is a low sulfur crude oil.

The chemical composition of crude can vary widely from different producing regions. Table 1 presents examples of the composition of crude oil from various regions including oil from South Louisiana and Prudhoe Bay (the source of the oil from the Exxon Valdez spill). South Louisiana crude is characterized by smaller fractions of sulfur, nickel, vanadium, naptha fractions (including aromatics) when compared to Prudhoe Bay or Kuwait crude oil. It is the lighter, more volatile, aromatic fractions that are of most concern as a health risk from an inhalational exposure.

# Table 1 Physical Characteristics and Chemical Properties of Several Crude Oils

Ref: Steering Committee for the Petroleum in the Marine Environment Update, Board on Ocean Science and Policy, Ocean Sciences Board, Commission on Physical Sciences, Mathematics and Resources, National Research Council. 1985. Oil in the Sea: Inputs, Fates, and Effects, The National Academies Press. Washington D.C.

Characteristic or Component	Prudhoe Bay	South Louisiana	Kuwait
API gravity (20° C)	27.8	34.5	31.4
Sulfur (wt %)	0.94	0.25	2.44
Nitrogen (wt %)	0.23	0.69	0.14
Nickel (ppm)	10	2.2	7.7
Vanadium (ppm)	20	1.9	28
Naptha fraction (wt %)	23.2	18.6	22.7
Paraffins	12.5	8.8	16.2
Naphthenes	7.4	7.7	4.1
Aromatics	3.2	2.1	2.4
Benzene	0.3	0.2	0.1
Toluene	0.6	0.4	0.4
C <sub>8</sub> aromatics	0.5	0.7	0.8
C <sub>9</sub> aromatics	0.06	0.5	0.6
C <sub>10</sub> aromatics		0.2	0.3
C <sub>11</sub> aromatics		0.1	0.1
Indans			0.1
High-boiling fraction (wt %)	76.8	81.4	77.3
Saturates	14.4	56.3	34.0
n-paraffins	5.8	5.2	4.7
C <sub>11</sub>	0.12	0.06	0.12
C <sub>12</sub>	0.25	0.24	0.28
C <sub>13</sub>	0.42	0.41	0.38
C <sub>14</sub>	0.5	0.56	0.44
C <sub>15</sub>	0.44	0.54	0.43
C <sub>16</sub>	0.5	0.58	0.45
C <sub>17</sub>	0.51	0.59	0.41
C <sub>18</sub>	0.47	0.40	0.35
C <sub>19</sub>	0.43	0.38	0.33
C <sub>20</sub>	0.37	0.28	0.25
C <sub>21</sub>	0.32	0.20	0.20
C <sub>22</sub>	0.24	0.15	0.17
C <sub>23</sub>	0.21	0.16	0.15
C <sub>24</sub>	0.20	0.13	0.12
C <sub>25</sub>	0.17	0.12	0.10
C <sub>26</sub>	0.15	0.09	0.09
C <sub>27</sub>	0.1	0.06	0.06
C <sub>28</sub>	0.09	0.05	0.06
C <sub>29</sub>	0.08	0.05	0.05
C <sub>30</sub>	0.08	0.04	0.07
C <sub>31</sub>	0.08	0.04	0.06
C <sub>32+</sub>	0.07	0	0.06
Isoparaffins		14.0	13.2
1-ring cycloparaffins	9.9	12.4	6.2
2-ring cycloparaffins	7.7	9.4	4.5

#### Weathering of the MC252 Crude

When crude oil is released in the environment, its composition changes as a result of "weathering." Weathering processes include evaporation and others. Evaporation occurs mainly during the first 24-48 hours after release which greatly reduces the amount of volatile components. Some crude oils may lose up to 40% of their volume due to evaporation in the first few days after a release. The substance remaining after evaporation is called weathered crude oil. Thus, the composition of any released product remaining in the affected area is likely to be substantially different than the originally released crude oil. Due to the weathering process, the remaining product is generally considered to have less potential for causing adverse health effects.

Unlike most previous oil spills, the MC 252 crude is being released into the environment at a depth of more than 5000 feet. In addition to evaporation of volatile components at the surface, as the crude passes through the water column to the surface there is some additional dissolution or chemical stabilization of oil components in the water. Table 2 shows the solubility of some of the common aromatic hydrocarbons found in water. The compounds with the greater solubility in water (Benzene, Toluene, Ethylbenzene, p-Xylene) will begin to dissolve into the water column prior to reaching the surface.

	Table 2
	Solubility of Some Aromatic Oil Compunds
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Ref: Mackay, D., W. Y. Shiu, and K. C. Ma. 1992. Illustrated handbook of physical chemical properties and environmental fate for organic chemicals, vol. 1. Monoaromatic hydrocarbons, chlorobenzenes and PCBs; also vol. II Polynuclear aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans, Lewis Publishers, Boca Raton, FL.

polychlorinated dioxins and dibenzolurans, Lewis Publishers, Boca Raton, FL.			
Compound	Solubility (mg/L)		
Benzene	1700		
Toluene	530		
Ethylbenzene	170		
p-Xylene	150		
Napthalene	30		
1-Methyl naphthalene	28		
1,3-Dimethyl naphthalene	8		
1,3,6-Trimehtyl naphthalene	2		
Fluourene	1		
Dibenzothiophene	1.1		
Chrysene	0.002		

#### Chemical Composition of MC252 Weathered Oil

A sample of MC252 weathered oil collected on April 27, 2010 was analyzed by Zymax Laboratory in Escondido, CA for whole oil analysis. The carbon range associated with the whole oil analysis is carbon-3 (C3) to carbon-44 (C44). In addition, the sample was analyzed by B&B Laboratories in College Station, Texas for polyaromatic hydrocarbons (PAHs).

The lowest molecular weight hydrocarbon detected in the whole oil analysis was the alkane *n*-C14 (labeled on the attached chromatogram). Naphthalene, a volatile PAH compound, elutes earlier than *n*-C14 and was not detected by Zymax but was present above detection limits at only 0.1 mg/kg oil using a more sensitive PAH method by B&B.

More volatile compounds, including benzene, toluene, ethylbenzene, and xylenes were also undetected.

#### **Zymax Laboratory Results**

Results from Zymax Laboratories indicate the weathered oil is comprised of aliphatic and cyclic hydrocarbons greater than C14. The results indicate that carbon compounds smaller than C14 are not detected and indicates the volatile fraction of the oil was rapidly lost to evaporation and dissolution prior to sampling.

The chromatogram presented in Figure 1 illustrates the distribution and relative abundance of aliphatic hydrocarbons in the weathered oil and that the lowest carbon number straight chain aliphatic hydrocarbon detected is C14. Lower carbon number aliphatics were analyzed for but not detected.

#### **B&B Laboratories Results**

Results from B&B Laboratories indicate that naphthalene, the lightest and most volatile cyclic hydrocarbon tested for in the PAH analysis, was detected slightly above the 0.1 mg/kg oil detection limit.

The chromatogram presented in Figure 2 illustrates the distribution and relative abundance of cyclic hydrocarbons in the weathered oil. Note that the concentration of naphthalene relative to the heavier cyclic hydrocarbons is so low that the bar graph for naphthalene does not appear.

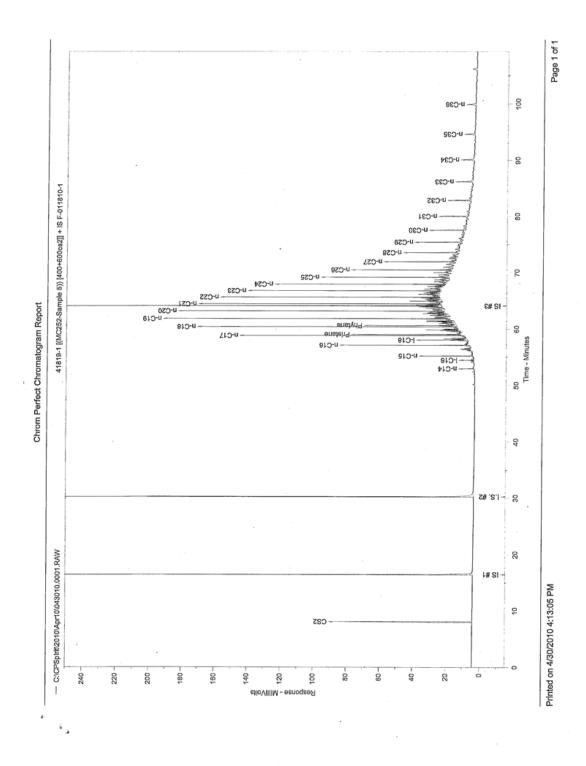
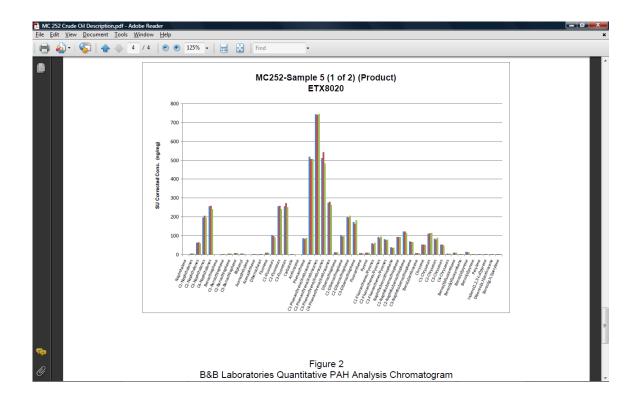


Figure 1
Zymax Laboratory Whole Oil Analysis Chromatogram



#### Chemistry of MC252 Crude Vapors

CTEH is in the process of identifying the chemical composition and concentration of crude oil vapors present in air from "fresh" crude oil based on laboratory data. The data obtained will be used to further guide decisions regarding potential chemicals of concern for the public and for workers engaged in cleanup activities.

On May 5, two SUMMA canisters were collected approximately 3 feet above the surface of fresh crude oil. Samples were analyzed by Pace Analytical using EPA Method TO-15 plus a request to identify what is called tentatively identified compounds or TICs. This method is used to identify the volatile phase of petroleum hydrocarbons.

On May 10, 4 SUMMA canisters and water samples were also collected from the Q-4000 (drill rig adjacent to the leaking well) and the BOA SUB C, ROV ship that is positioned directly above the oil source. Air samples were collected immediately above the surface of fresh crude and on the deck of the ship vessel (representative of worker locations). These samples were also analyzed by Pace Analytical.

The results of chemical analysis for several of the components of interest have been extracted from the analytical reports and summarized in Table 3 below. Results are significantly below OSHA PELs for benzene, toluene, and xylene at the water surface and are even lower at deck levels representative of worker

positions. As discussed previously, the results are consistent with crude oil vapors travelling through more than a mile of seawater where the more water soluble compounds tend to go into solution and the less soluble, smaller molecular weight compounds volatilize into the atmosphere upon reaching the surface. Since these samples are taken at the source of the leak and with "fresh" oil, it would be expected that air exposures for shore-based workers would be significantly less.

Table 3 Summary of Extracted Air Sample Results fro SUMMA Canisters					
Ref: CTEH Report on Preliminary Evaluation of Crude Oil and Vapor Phase Analytical Findings, May 11, 2010.					
Compound	Sample Concentration 3' Above Water Surface (ppbv)	Sample Concentration Vessel Deck Level / Representative Worker Locations (ppbv)			
Benzene	ND – 4.8	ND			
Toluene	4.6 – 25.4	ND			
Ethylbenzene	1.6 – 10.8	ND			
m&p-Xylenes	8.0 – 70.8	3.7			
o-Xylene	2.6 – 27.3	1.5			
THC as Gas	645 – 5550	847			

### Air Sampling for Worker Protection

OSHA receives daily air sample results and reports from BP and their contractors. The data is received as raw results and as summary reports. A Certified Industrial Hygienist with the Health Response Team (HRT) is reviewing the sample results and reports on a daily basis to identify potential issues. OSHA also receives daily sample results from EPA. EPA has provided the HRT with direct access to their scribe database for review of air, water, and sediment sample results as sample results are added to the database. A brief summary of some of the sampling results is presented below.

#### Shore-based Area Air Sampling

The Center for Toxicology and Environmental Health (CTEH) has been contracted by BP to conduct area sampling for benzene, hydrogen sulfide, sulfur dioxide, and volatile organic compounds in residential and commercial areas along the Gulf coast. From April 29 – May 15, CTEH has taken 12,830 measurements. A review of the data demonstrates:

- 418 measurement for benzene with all results below the detection limit
- 5,980 measurements for hydrogen sulfide with all results below the detection limit

 6,432 measurements for volatile organic compounds with the highest result being 0.4 ppm

#### Vessel Area Air Sampling

Total Safety, Inc. has been contracted by BP to conduct area sampling for combustible gas, oxygen, hydrogen sulfide, carbon monoxide, and volatile organic compounds on vessels conducting source control and skimming operations. The action level for chemicals include:

- Volatile Organic Compounds -100 ppm for 15-minutes
- Hydrogen Sulfide 5 ppm for 15-minutes
- Benzene 0.5 ppm for 3 samples for 15 minutes
- Carbon monoxide 25 ppm for 15 minutes

Work areas on the vessel are monitored each day initially and at regular intervals while operations are being conducted. The frequency of monitoring is also increased if conditions change (such as a change in the amount of oil in the area, shift in wind direction, or change in readings from direct reading instruments). A combination of continuous and instantaneous samples are taken throughout the day. A review of the data for seventeen vessels from April 29 – May 12, showed the following:

- Several thousand data points and sample results were reviewed by the HRT on over 17 vessels
- There were no instances of exceeding the action levels identified above for volatile organic compounds, hydrogen sulfide, benzene, or carbon monoxide.

#### Monitoring of Personnel on Vessels

Total Safety, Inc. has been contracted by BP to conduct personal sampling for benzene and other hydrocarbons for workers on vessels conducting source control and skimming operations. Organic Vapor Monitor (OVM) badges are placed on workers identified as having the highest potential for exposure. The badges are analyzed by Bureau Veritas, an AIHA accredited laboratory using OSHA method 7. A review of the results for samples taken from April 27 – May 3 showed the following:

- 64 personal samples were collected
- All sample results for benzene were less than 0.055 ppm. The OSHA PEL is 1.0 ppm.
- All sample results for ethyl benzene were less than 0.075 ppm. The OSHA PEL is 100 ppm.
- All sample results for toluene were less than 0.079 ppm. The OSHA PEL is 200 ppm.
- All sample results for xylene were less than 0.57 ppm. The OSHA PEL is 100 ppm.

### Air and Water Sampling for Dispersant

Bureau Veritas and EPA's ERT will separately conduct area air monitoring for COREXIT 9500 and EC9527A dispersant beginning May 16 for 3 days (weather permitting for dispersant application). Samples will be taken from the deck of ships nearest closest to where the dispersant is applied to determine a worst case scenario. Additional samples will be taken at several shoreline locations downwind of dispersant application. EPA's TAGA bus will also conduct real-time monitoring starting May 17.

Samples will be analyzed for 2-butoxyethanol, propylene glycol and volatile organic compounds (principal components of the dispersant). Samples will be collected via charcoal tubes, XAD-7 OVS tubes, and SUMMA canisters for laboratory analysis.

Surface and subsurface water samples will also be collected and analyzed for dispersant both at sea where the dispersant is being applied and at shoreline locations.

#### Role of SCAT Teams in Shoreline Cleanup

Shoreline Cleanup and Assessment Teams (SCAT) are composed of federal, state and BP officials that work to assess and determine where and how cleanup will be conducted and oversee cleanup operations. Prior to workers being deployed to areas for cleanup, SCAT teams conduct and initial assessment.